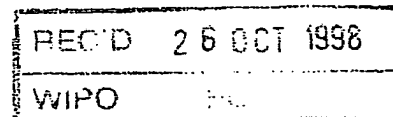




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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

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FUNCTIONALIZED POLYMERS

The invention relates to a new process for functionalizing polymers prepared by carbocationic polymerization, and to new functionalized polymers, such as telechelic prepolymers.

5 Polymers having functional groups are useful as lube additives, compatibilisers, emulsifiers or as raw material for the production of adhesives, modifiers, coating material, sealing material and the like. Consequently, there has been a lively interest in
10 functionalized polymers.

 Carbocationic polymerization is one of the known routes for preparing functionalized polymers. For instance, WO 94/13706 discloses a method for direct synthesis by living cationic polymerization of novel
15 polymeric materials functionalized with nitrogen-containing functional groups. Polymerization and functionalization occur in a substantially simultaneous manner (e.g., in a one-step Friedel-Crafts reaction). In section II.5.2 of the textbook "Designed Polymers by
20 Carbocationic macromolecular Engineering: Theory and Practice" (Hanser Publishers, 1991) the authors J P Kennedy and B Iván provide numerous examples with additional end-groups both in polyolefins and poly(alkyl vinyl ether)s, albeit typically in a two-step process.

25 It will be understood that polymers prepared in a one-step carbocationic polymerization process having novel end-groups, with potential for further reactions, will be highly desired.

 Accordingly, a process has now been found for
30 functionalizing polymers prepared by carbocationic

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polymerization wherein a living carbocationic polymerization system is reacted with one or more aromatic ring systems.

5 The process is particularly suitable when the one or more aromatic ring systems are selected from five-, six- or seven-atom heterocycles. Such heterocycles will have one or more heteroatoms selected from N, O, P and S and typically provide the necessary electron-rich environment required for the reaction, a Friedel-Crafts reaction, to
10 occur. Preferably, the one or more aromatic ring systems are selected from six- π -electron ring systems. Examples of particularly preferred aromatic ring systems include pyrrole, furan, thiophene, oxazole, isothiazole, 1,3,4-thiadazole, and pyrazole. These aromatic ring
15 systems may be substituted in part, provided the substituents neither sterically block the remaining reactive sites of the aromatic ring systems, nor deactivate the aromatic ring systems. For instance, the substituents may be selected from amino, hydroxy, alkoxy, aminocarbonyl, alkyl or aryl groups, or halogen atoms.
20 The first mentioned substituents are the stronger activating groups. Such substituents may be relatively large, e.g., in case the aromatic ring system acts as a coupling agent, the first substituent corresponds (on average) to half the molecular weight of the functionalized polymer. Examples of suitable substituted aromatic
25 ring systems include for instance 3,3-dimethyl-3H-pyrazole and 2,2-bithienyl.

30 The one or more aromatic ring systems may also be selected from (benzo-)fused ring systems, such as naphthalene, quinoline, quinoxaline, indole, the benzofurans, the benzothiophenes, pteridine, purine, indolizine and the like. Again, these one or more aromatic ring systems may be substituted in part with the
35 same substituents mentioned above.

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Preferably, the one or more aromatic ring systems are selected from pyrrole, furan and thiophene and substituted versions thereof. The polymers thus prepared can be further functionalized through the well known and very extensive chemistry of the pyrrole, furan and thiophene structure. An additional advantage of the use of thiophene or a substituted thiophene is the inherent anti-oxidant properties of the functionalized polymer.

Note that, as used throughout this specification, the definition of living polymers coincides with that of WO 94/13706 and the textbook by Kennedy and Iván mentioned above. Thus, living carbocationic polymerization systems comprise ideal living polymerizations, based on cationic initiation in which chain transfer and termination are absent and quasi living polymerizations in which rapidly reversible chain transfer and/or termination are present and the rate of these processes is faster than that of propagation. In other words, systems wherein the rate of irreversible chain transfer and/or termination is zero or appears to be zero.

As is discussed in the textbook, (living) carbocationic polymers are polymers formed by controlled initiation, i.e., by an initiator that is either monofunctional or polyfunctional, whereby the polymer chain will propagate at one end in one direction or from the centre in more directions.

Suitable living carbocationic polymerization systems are, for instance: t-alkyl esters/ BCl_3 ; cumyl acetate/ TiCl_4 ; 2,2'-bipyridyl/ TiCl_4 ; $\text{CH}_3\text{SO}_3\text{H}/\text{SnCl}_4$ + $\text{n-Bu}_4\text{NCl}$; HI/I_2 ; HI/ZnX_2 or SnX_2 ($\text{X} = \text{Cl}, \text{Br}$); HI/ZnI_2 ; or $\text{CH}_3\text{COClO}_4$ using as monomer(s) for instance: isobutene; isobutene/2,4-dimethyl-1,3-pentadiene; styrene; p-vinyl-phenyl glycidyl ether; isobutyl vinyl ether; methyl vinyl ether/p-methoxystyrene; or 2-methyldihydrofuran, respectively (for a more comprehensive list see Table IV,

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pp. 43-55 of the aforementioned textbook). In addition, the nitrogen-containing compounds employed as initiator in WO 94/13706 may be used, such as 2-azido-isopropylbenzene or bis(2-azido-isopropyl)benzene in admixture with diethylaluminium chloride, TiCl_4 or BCl_3 .

Although insoluble catalysts may be used, preferably homogeneous catalysts are used. It is common to use solvents in the polymerization process. Suitable solvents have a freezing point (well) below the preferred polymerization temperature. Illustrative solvents include, but are not limited to, C_2 to C_{10} alkanes, -alkenes and -alkylhalides and -alkenylhalides, carbon tetrachloride, carbon disulphide, nitroethane, liquid carbon dioxide and methylcyclohexane. Mixed solvents can also be used. The preferred solvents are the low-boiling alkylhalides; chloroform, methylene dichloride, methyl chloride, ethyl chloride, propyl chloride, n-butyl chloride, and 1,2-dichloroethane, and neopentane, hexane, heptane and purified petroleum ether.

Any cationically polymerizable monomer may be used, including straight and branched chain alpha-olefins, isoolefins, alicyclic monoolefins, cycloaliphatic compounds, styrene derivatives, indene and derivatives, and other monoolefins and heterocyclic cationically polymerizable monomers identified in the text by Kennedy, "Cationic Polymerization of Olefins: A Critical Inventory"; pp. 39-53; Wiley, 1975). Vinyl ethers can also be used.

Particularly valuable polymers can be prepared from isoolefins of from 4 to 20 carbon atoms or mixtures thereof. Examples of such unsaturated hydrocarbons include, but are not restricted to, isobutene, 2-methylbutene, 3-methyl-1-butene, 4-methyl-1-pentene, and beta-pinene. Other cationically polymerizable monomers that may be employed include heterocyclic monomers such as

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oxazolines and others known to add onto polarized covalent bonds. Mixtures of cationically polymerizable monomers can be employed as feedstock to the polymerization zone if desired. Thus, copolymers, terpolymers and higher interpolymers can be prepared by employing a mixture of two, three or more of the above monomers. Preferred feedstocks to the polymerization zone comprise pure isobutene and mixed C₄ hydrocarbon feedstocks containing isobutene, such as a C₄ cut resulting from the thermal or catalytic cracking operation of, for example, naphtha. Suitable isobutene feedstocks will typically contain at least 10%, and up to 100% isobutene by weight on the weight of the feed. Conventional C₄ cuts suitable for use as a feedstock, which are of industrial importance, typically will contain between 10 and 40% 1-butene, between 10 and 40% 2-butene, between 40 and 60% isobutane, between 4 and 10% n-butane, and up to about 0.5% butadiene, all percentages being by weight based on the feed weight. Feedstocks containing isobutene may also contain other non-C₄ polymerizable olefin monomers in minor amounts, e.g. typically less than 25%, preferably less than 10%, and most preferably less than 5%, such as propadiene, propylene and C₅ olefins. The term "polyisobutene" as employed herein is intended to include not only homopolymers of isobutene but also copolymers of isobutene and one or more other C₄ polymerizable monomers of conventional C₄ cuts as well as non-C₄ ethylenically unsaturated olefin monomers containing typically from 3 to 6, and preferably from 3 to 5 carbon atoms, provided such copolymers contain typically at least 50%, preferably at least 65%, and most preferably at least 80% isobutene units, by weight, based on the polymer number average molecular weight (M_n). The substantially selective polymerizability of isobutene under the

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conditions specified herein ensures that minimum isobutene content described above.

Preferably the polymerization medium is substantially free of poisons to the catalyst. For instance, the olefin feed can be treated by use of mole sieves and subjected to caustic washing to remove, e.g., mercaptans, water, and dienes (if desired).

The polymerization reaction may be conducted batchwise, or in a (semi)continuous operation in which continuous streams of ingredients are delivered to the reactor and an overflow of a slurry or solution of polymer is taken out for the recovery of the polymer therefrom. From an operational point of view, the preferred mode of reaction is on a continuous basis using a continuous flow stirred reactor wherein, in a controlled manner, feed is continuously introduced into the reactor and product is continuously removed from the reactor. However, in case a more well defined (narrow molecular weight distribution) product is to be produced, a batch process is preferred.

The amount of catalyst employed in the process of the present invention can be varied to achieve the target number average molecular weight of polymer. Varying the amounts may also minimize or reduce undesired isomerizations. The lower the initiator concentration in the reaction phase, the higher will be the polymer molecular weight and vice versa. Control of the polymer molecular weight within defined limits of a selected target polymer molecular weight is particularly important when the polymer is intended for use in lubricating oils as a dispersant. The catalyst amount also affects the conversion of the olefin monomer and yield of polymer, with higher amounts of catalyst typically achieving higher conversion and yields. The catalyst should be

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employed in sufficient amount to enable the reaction to be a "living" cationic polymerization.

The polymerization reaction is conducted in the liquid phase to induce linear or chain type polymerization instead of ring or branch formation. If a feed is used which is gaseous under ambient conditions, it is preferred to control the reaction pressure and/or dissolve the feed in an inert solvent or liquid diluent, in order to maintain the feed in the liquid phase.

Typical C₄ cuts used as feed are liquid under pressure and do not need a solvent or diluent. If under normal circumstances the selected catalyst is a gas (e.g. BF₃ and the like) the gaseous catalyst is typically partially or completely dissolved in a pressurized liquid after introduction in the reactor. Polymerization pressures can range typically from 25 to 500, and preferably from 100 to 300 kPa.

The temperature at which the polymerizations are carried out is important, since temperatures that are too high tend to decrease the functionalization degree. The usual polymerization temperature range is between -100 °C and +10 °C. Preferably, the polymerizations are performed at a temperature below -10 °C, preferably below -20 °C, and preferably between -80 °C and -20 °C, e.g. at a temperature of -50 °C. The liquid phase reaction mixture temperature is controlled by conventional means. The particular reaction temperature is selected to achieve the target living polymerization behaviour, and preferably is not allowed to vary more than + or - 5 °C from the selected value, while the catalyst and/or promoter feed rate is varied to achieve the desired Mn to compensate for variations in monomer distribution in the feed composition.

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Average polymerization times, in minutes, can vary from 10 to 120, preferably from 15 to 45 (e.g. 20 to 30), and most preferably from 15 to 25.

5 The reaction, which is a Friedel-Crafts alkylation reaction, will occur under the same conditions required to form the carbocationic polymerization system. These conditions will therefore be readily familiar to the persons skilled in this art. Besides, Friedel-Crafts alkylation reactions are well-known and examples of
10 suitable conditions and references to further examples may, for instance, be found in "Advanced Organic Chemistry" by J March (section 1-13 of 3rd edition; Wiley, 1985). Typical conditions involve some form of temperature control to remove the heat of reaction, a
15 solvent and a means to bring the reagents into contact (stirrer, etc.).

The materials used to quench the reaction are conventional and include the same materials commonly used as cationic polymerization promoters (e.g. moisture,
20 alcohol) with the exception that excess quantities are employed in amounts sufficient to deactivate the catalyst. Thus, while any amount of quenching medium effective to deactivate the catalyst may be employed, it is contemplated that such effective amount be sufficient
25 to achieve a molar ratio of quench medium to catalyst of typically from 1:1 to 100:1, preferably from 3:1 to 50:1, and most preferably from 10:1 to 30:1. Quench is conducted by introducing the quench medium into the polymer product. Typically, the polymer product is maintained
30 under pressure during the quench sufficient to avoid vaporisation of any gaseous catalyst (if one is employed) and other components of the mixture. The temperature of the quenching medium is not critical and, e.g. can comprise room temperature or lower. In a batch system,
35 quench can be performed in the reactor or preferably on

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the product after it is withdrawn from the reactor. In a continuous system, the quench will typically be performed after product exits the reactor. After quench, the polymerization product is typically subjected to conventional finishing steps that include a caustic/H₂O wash to extract catalyst residue, a hydrocarbon/aqueous phase separation step wherein deactivated and extracted catalyst is isolated in the aqueous phase, and a water washing step to remove residual amounts of neutralized catalyst. The polymer is then typically stripped in a debutanizer to remove unreacted volatile monomers, followed by a further stripping procedure to remove light end polymer (e.g. C₂₄ carbon polymer). The stripped polymer is then typically dried by N₂.

In principle, the one or more aromatic ring systems may be introduced during the preparation of the carbocationic polymerization system, although a better defined product is prepared when the living carbocationic polymerization systems have exhausted the supply of monomers. Depending on the ratio of living carbocationic polymerization systems per amount of one or more aromatic ring systems, and depending on the functionality of the initiating system, polymers may be prepared having the functional end-group at one terminus of the polymer chain (1:1; monofunctional), having the one or more aromatic ring systems coupling two or more living carbocationic polymerization systems (so-called branched or star-branched polymers prepared e.g., in a ratio of 2 or more:1; monofunctional) having living carbocationic polymerization systems end-capped at some or each of the propagating termini (so-called telechelic prepolymers prepared e.g., in a ratio of 2:1; bifunctional or 3:1; trifunctional, etc.), and even mixed systems where the one or more aromatic ring systems act as both coupling agent and as functional end-group when a polyfunctional

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initiator is used. Examples include, but are not limited to:

I-P-Ar

I-P-Ar-(P-I)_n

5 Ar-P-I'-(P-Ar)_m

Ar-P-I''-P-Ar-P-I''-P-Ar

wherein Ar represents the one or more aromatic ring systems, P represents the polymer (e.g., homopolymer, random or block copolymer, etc.), I represents the monofunctional initiator, I' represents the polyfunctional, II' represents the bifunctional initiator, and n and m are numericals corresponding to the functionality of the one or more aromatic ring systems, or the polyfunctional initiator, respectively.

15 In particular the telechelic prepolymers and the branched or star-branched polymers capped by more than one functional terminal groups are useful in the preparation of high molecular weight products, including networks and VI improvers.

20 The reaction products of the present invention may be used as a dispersant additive in lubricating oils. Accordingly, the present invention provides a lubricating oil composition comprising a major amount (more than 50 %w) of a lubricating oil and a minor amount (less than 50 %w), preferably from 0.1 to 20 %w, especially from 0.5 to 10 %w (active matter), of a reaction product according to the present invention, the percentages by weight being based on the total weight of the composition.

25 30 Suitable lubricating oils are natural, mineral or synthetic lubricating oils.

Natural lubricating oils include animal and vegetable oils, such as castor oil. Mineral oils comprise the lubricating oil fractions derived from crude oils, coal or shale, which fractions may have been subjected to certain treatments such as clay-acid, solvent or

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hydrogenation treatments. Synthetic lubricating oils include synthetic polymers of hydrocarbons, modified alkylene oxide polymers, and ester lubricants, which are known in the art. These lubricating oils are preferably crankcase lubricating oils for spark-ignition and compression-ignition engines, but include also hydraulic lubricants, metal-working fluids and automatic transmission fluids.

Preferably the lubricating base oil component of the compositions according to the present invention is a mineral lubricating oil or a mixture of mineral lubricating oils, such as those sold by member companies of the Royal Dutch/Shell Group under the designations "HVI", or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark).

The lubricating oil compositions of the invention may be prepared by adding the reaction products of the present invention to a lubricating oil. Conveniently, an additive concentrate is blended with the lubricating oil. Such a concentrate generally comprises an inert carrier fluid and one or more additives in a concentrated form. Hence the present invention also provides an additive concentrate comprising an inert carrier fluid and from 10 to 80 %w (active matter) of a reaction product according to the present invention, the percentages by weight being based on the total weight of the concentrate.

Examples of inert carrier fluids include hydrocarbons and mixtures of hydrocarbons with alcohols or ethers, such as methanol, ethanol, propanol, 2-butoxyethanol or methyl tert-butyl ether. For example, the carrier fluid may be an aromatic hydrocarbon solvent such as toluene, xylene, mixtures thereof or mixtures of toluene or xylene with an alcohol. Alternatively, the carrier fluid may be a mineral base oil or mixture of mineral base oils, such

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as those sold by member companies of the Royal Dutch/Shell Group under the designations "HVI", e.g. "HVI 60" base oil, or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark).

The present invention still further provides the use of a reaction product according to the present invention as a dispersant additive.

The following examples illustrate the invention. Examples 1 to 5 are model experiments. They use a living carbocationic dimerisation system derived from 2-chloro-2,4,4-trimethylpentane, thus resembling the dimer of isobutene, instead of a living carbocationic polymerization system as reagent. Examples 6 to 10 illustrate products of the invention using polyisobutene as polymeric component. Finally, example 11 concerns the antioxidancy test of a thiophene-functionalized PIB, illustrative for a potential, interesting outlet of the novel products of the invention, whereas example 12 illustrates the properties of functionalized PIBs as dispersant.

Typically, the examples were conducted in a batch reactor dipped in an external cold bath. Solvents and reagents were all thoroughly dried. In the examples the following abbreviations are used:

CTMP	2-chloro-2,4,4-trimethylpentane
tmb	1,1,3,3-tetramethylbutyl (radical)
PIB	polyisobutene or its radical
MCH	methylcyclohexane
DCM	dichloromethane
MeOH	methanol
TH	Thiophene
BrTH	2-bromothiophene
MeTH	2-methylthiophene

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BTH 2,2'-bithienyl
 DBTH 3-dodecyl-2,2-bithienyl
 DTHCE 1,1-di(2-thienyl)-2,2,2-trichloroethane
 FU furane
 5 Me-FU 2-methylfurane
 DtBP 2,6-di-tert.-butylpyridine.

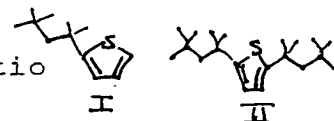
Synthesis DBTH

DBTH is prepared by reaction of 3-bromoBTH with dodecyl magnesium bromide. 3-BromoBTH is prepared by reacting 2-thiophene magnesium bromide with BrTH in the presence of 1,1'-bis(diphenylphosphino)ferrocene.

Example 1

In a three necked round bottom 250 ml flask, equipped with a magnetic stirrer 305 mg (2.05 mmol) CTMP is introduced followed by 40 ml of 60:40 v/v MCH/DCM and 1385 mg (10.02 mmol) of cis-decaline (internal standard). The reactor is then cooled down to -80 °C, whereupon 1869 mg (9.85 mmol) TiCl₄ dissolved in 40 ml MCH/DCM is added. Next 90 mg (1.07 mmol) TH dissolved in 20 ml MCH/DCM is added. At intervals 2 ml samples are taken, that are quenched with 2 ml MeOH at -80 °C and analysed by gas liquid chromatography.

GLC revealed the conversion grade and the ratio between the end-capped and coupled products, 2-(tmb)TH (I) and 2,5-bis(tmb)TH (II). After a period of 2 hours, the conversion grade reached 60 % (on intake TH) and a product ratio I/II of 83/17. After a night stirring allowing for the mixture to warm up to room temperature a conversion of 97.4 percent was reached at a ratio of 54/36.

Example 2

Under conditions similar to Example 1 no reaction took place when TH was replaced with 1.28 g (10 mmol)

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2-acetylTH. Obviously, the 2-acetyl group is a deactivating group.

Example 3

Under conditions similar to Example 1, 1.32 g 2-methyl-5(tmb)FU is produced (conversion of 68%) in half an hour when the TH is replaced by 0.82 g (10 mmol) of 2-methylFU. The following analytical data were found:

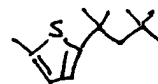
$^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.76 (s, 9H), 1.29 (s, 6H), 1.63 (s, 2H), 2.26 (d, 3H), 5.82 (m, 2H);

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 14.0, 30.1, 31.2, 32.0, 5.9. 54.8, 104.0, 106.0, 150.1, 161.4 ppm.

Example 4

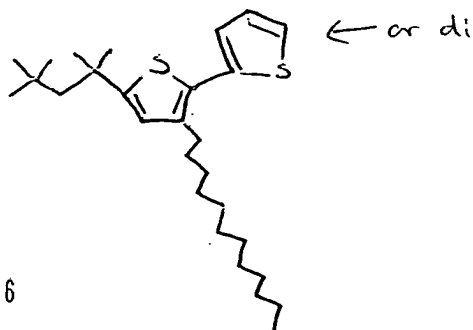
In a three necked round bottom 250 ml flask, equipped with a magnetic stirrer 7.55 g (51 mmol) CTMP is introduced followed by 5.0 g (51 mmol) 2-methylTH dissolved in 20 ml of DCM. Slowly 0.870 g (6.13 mmol) $\text{BF}_3 \cdot \text{OEt}_2$ is added and the reaction is followed by GLC. According to the GLC data the monoalkylation product was immediately formed after addition of the Lewis acid, with some minor dialkylation product being formed.

The crude product is washed, dried and subjected to partial distillation (Kugelrohr). A conversion of 19 percent of 2-methylTH into 2-methyl-5(tmb)TH was found.

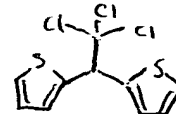
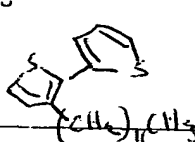


Example 5

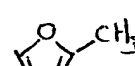
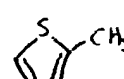
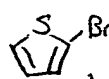
The procedure of Example 1 is followed using 0.555 g (3.75 mmol) CTMP dissolved in 10 ml 40:60 v/v hexane:DCM; 3.55 g (18.75 mmol) TiCl_4 dissolved in 20 ml of said solvent; and 0.60 g (1.875 mmol) of DBTH dissolved in 20 ml of said solvent. The progress of the reaction is determined by GC wherein two separate peaks of equal size are identified, shown (by GC-MS) to be related to 5-(tmb)DBTH and 5'-(tmb)DBTH. A conversion of 75 % was achieved.



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Example 6

PIB-functionalization experiments have been carried out with TH, BrTH, MeTH, DTHCE, DBTH, FU, and MeFU.

The isobutene polymerizations were carried out by a simple laboratory polymerization process in a CH_2Cl_2 /hexane solvent mixture at -78°C . The aromatic ring systems were added after reaching high ($\sim 100\%$) monomer conversion. The changes in the structure of the chain ends were investigated by UV spectroscopic detector during GPC runs and by ^1H NMR spectroscopy.

The experimental conditions for the end-capping with BrTH is as follows: The reactor is filled with 6.2 mmol CTMP, 5.2 mmol 2,2'-bipyridyl, 150 ml CH_2Cl_2 and 350 ml hexane. This solution is cooled to -78°C , whereupon 5 ml IB is added followed by 100 ml TiCl_4 dissolved in CH_2Cl_2 (0.18 M). 5 and 10 minutes later a further 4 ml IB were added. When the polymerization was completed, 31 mmol BrTH dissolved in 100 ml (prechilled) CH_2Cl_2 was added thereto and the reaction was monitored over time (using prechilled methanol as quenching agent).

The experimental conditions for the end-capping with MeTH is as follows: The reactor is filled with 3.6 mmol CTMP, 2.4 mmol 2,2'-bipyridyl, 50 ml CH_2Cl_2 and 140 ml hexane. This solution is cooled to -78°C , whereupon 5 ml IB is added followed by 50 ml TiCl_4 dissolved in CH_2Cl_2 (0.24 M). 5 and 10 minutes later a further 5 ml IB were added. When the polymerization was completed, 10 mmol MeTH dissolved in 50 ml (prechilled) CH_2Cl_2 was added thereto and the reaction was monitored over time (using prechilled methanol as quenching agent).

Both BrTH and MeTH resulted in quantitative conversion of the chain ends of polyisobutene (PIB) to the corresponding heterocyclic functionalities. The reaction between the carbocationic chain ends and these compounds are relatively fast processes; UV analysis

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indicated quantitative conversion in 30 to 45 minutes with BrTH, respectively 10 to 20 minutes with MeTH.

¹H NMR spectra show signals at 6.55 (d, 2H), 6.80 (d, 2H) for 2-bromo-thiophene and 6.50 (d, 2H), 6.55 (d, 2H) for 2-methyl-thiophene, which illustrates the formation of the corresponding chain ends upon functionalization with BrTH and MeTH, respectively. It is noteworthy that aromatic signals appear for the heterocyclic chain ends, and there is no signal at 1.94 ppm for the -CH₂- group characteristic for the tertiary chlorine chain end in PIBs quenched with nucleophiles not reacting with the cationic chain ends. The spectroscopic results (UV and NMR) indicate quantitative end-quenching with BrTH and MeTH.

Coupling of living PIB chains was also attempted by bisthienyls. UV signals in GPC indicate efficient addition of the bisthienyls to the chain ends. However, molecular weight data confirm neither DBTH nor DTHCE let to coupling of the chains. Warming up the polymerization system to room temperature in the presence of DBTH did not lead to coupling either.

It was also found by preliminary experiments that furan and 2-methylfuran also react with the living PIB chains. However, optimization of these reactions and detailed characterization of the formed products require further systematic studies.

Example 7

The isobutene polymerization was carried out at -78 °C using 33 mmol CTMP, 49 mmol DtBP and 131 mmol TiCl₄ as initiating system; 600 ml of 60:40 v/v MCH/DCM as solvent and 1114 mmol IB. After 1 hour 31 mmol MeTH was added. A quantitative conversion was found into 2-methyl-5(PIB)TH in 30 minutes.

Example 8

The isobutene polymerization was carried out at

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-78 °C using 16.5 mmol CTMP, 4.2 mmol DtBP and 63 mmol TiCl_4 as initiating system; 600 ml of 60:40 v/v MCH/DCM as solvent and 604 mmol IB. The polymer formed had a number average molecular weight of 2244. After 1 hour 7.3 mmol TH was added. A quantitative conversion was found in 30 minutes. The product was determined to comprise both 2-(PIB)TH (Mn of 2575) and 2-5-di(PIB)TH (Mn of 3121).

Example 9

The isobutene polymerization was carried out at -78 °C using 16.8 mmol CTMP, 24 mmol DtBP and 65 mmol TiCl_4 as initiating system; 600 ml of 60:40 v/v MCH/DCM as solvent and 566 mmol IB. After 0.5 hour 21 mmol MeFU was added. A quantitative conversion was found into 2-methyl-5(PIB)FU in 30 minutes.

Example 10

The isobutene polymerization was carried out at -78 °C using 60 mmol CTMP, 30.1 mmol 2,2'dipyridyl and 562.5 mmol TiCl_4 as initiating system; 1200 ml of 60:40 v/v MCH/DCM as solvent and 916 ml IB. After 1 hour 50% of the solution is removed. To the remaining solution 60 mmol ethyl-2-thiopheneacetate was added. After 2 hours GPC, ^1H and ^{13}C -NMR confirmed the presence of the desired functionalized PIB.

Example 11

A fully formulated oil (comprising dispersant, detergent, zinc dithiophosphate as extreme pressure anti-wear agent, and 1 %wt of 2-methylthienyl capped PIB of Mn of 1500 or 3500 respectively) was subjected to an anti-oxidancy test using isothermal Differential Scanning Calorimetry (DSC) analysis.

The analysis was carried out using two Mettler-Toledo instruments (DSC27HP). Thus, a 2.00 ± 0.05 mg of sample was placed in an aluminium pan and loaded into the DSC apparatus. Oxygen pressure and flow rate were then set to

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3.4 MPa (500 psig) and 60 normal ml/min respectively using Brooks pressure and mass flow controllers. The sample was rapidly heated to the test temperature of 200 °C by overriding the ramp rate control. Power output was then monitored while holding the sample at the test temperature. The induction period was measured by taking the intercept of the tangent to the point of maximum slope on the rising side of the exothermic peak, identified by taking the derivative of the enthalpogram, with the baseline.

The test revealed the samples to have a mean induction period of 13.7 respectively 13.6 minutes as compared to a mean induction period of 10.9 minutes for the formulated oil without the 2-methylthienyl capped PIB.

In other words, these 2-methylthienyl capped PIBs are effective antioxidants.

Example 12

The product of example 10 (Mn = 3180; 3.0 mmol) and N,N-dimethyl-1,3-diaminopropane (DAP; 150 mmol) were placed in a three neck flask with reflux condenser and heated for 10 hours at 130 °C. The excess of DAP was removed under vacuum. The reaction mixture was diluted with hexane (60 ml) and washed with methanol (3x 30 ml). The organic layer was dried over MgSO₄ and filtered. The solvent was removed leaving a highly viscous material. Yield: 75%.

¹³C-NMR: clear sign of bonded thienyl and bonded DAP carbons at 170.1, 157.7, 133.4, 126.5 and 122.2 ppm, and 58.8, 58.4 and 45.3 ppm, respectively.

IR: clear sign of amide carbonyl at 1660 cm⁻¹ and no ester carbonyl.

Element analysis: 1.07 %w N, 0.90 %w S.

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This polymer, at 2 %w active matter in HVI-65 NS base stock, reduces the viscosity of a 4.76 %w carbon black dispersion at 100 °C by 66% at a shear rate of 0.2 s⁻¹.

5 In other words, these functionalized PIBs are effective dispersants.

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TS 0436 EPCC L A I M S

1. A process for functionalizing polymers prepared by carbocationic polymerization wherein a living carbocationic polymerization system is reacted with one or more aromatic ring systems.

5 2. A process as claimed in claim 1, wherein the one or more aromatic ring systems are selected from five-, six- or seven-atom heterocycles.

10 3. A process as claimed in claim 2, wherein the one or more aromatic ring systems are heterocycles comprising one or more heteroatoms selected from nitrogen, oxygen, phosphor or sulphur.

4. A process as claimed in claim 1 or 2, wherein the one or more aromatic ring systems are selected from six- π -electron ring systems.

15 5. A process as claimed in any of the preceding claims, wherein the one or more aromatic ring systems are selected from the heterocycles pyrrole, furan, thiophene, oxazole, isothiazole, 1,3,4-thiadazole, pyrazole, from the substituted version of these heterocycles and from
20 the substituted or unsubstituted (benzo-)fused version of these heterocycles, provided the substituents, if any, neither sterically block the remaining reactive sites of the aromatic ring systems, nor deactivate the aromatic ring systems.

25 6. A process as claimed in any of the preceding claims, wherein the one or more aromatic ring systems are selected from heterocycles pyrrole, furan, thiophene, and from the substituted version of these heterocycles, provided the substituents, if any, neither sterically
30 block the remaining reactive sites of the aromatic ring systems, nor deactivate the aromatic ring systems.

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7. A process as claimed in claims 5 or 6, wherein the substituents are amino, hydroxy, alkoxy, aminocarbonyl, aryl or alkyl groups, or halogen atoms.

5 8. Telechelic prepolymers that are capped by one or more functional terminal groups, wherein the terminal groups are five-atom, six- π -electron heterocycles.

10 9. Branched or star-branched polymers that are coupled by one or more polyfunctional coupling groups, wherein the polyfunctional coupling groups are five-atom, six- π -electron heterocycles.

10. Branched or star-branched polymers as claimed in claim 9 that are capped by one or more functional terminal groups, wherein the terminal groups are five-atom, six- π -electron heterocycles.

15 11. A lubricating oil composition comprising a major amount of a lubricating oil and a minor amount of a reaction product according to the process of any one of claims 1 to 7.

20 12. An additive concentrate comprising an inert carrier fluid and from 10 to 80 %w, based on the total concentrate, of a reaction product according to the process of any one of claims 1 to 7.

13. Use of a reaction product according to the process of any one of claims 1 to 7 as a dispersant additive.

25 14. The use of telechelic prepolymers as claimed in claim 8 or branched or star-branched polymers as claimed in claim 10 in the preparation of high molecular weight products, including networks and HI improvers.

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FUNCTIONALIZED POLYMERS

A process for functionalizing polymers prepared by carbocationic polymerization wherein a living carbocationic polymerization system is reacted with one or more aromatic ring systems.

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